NOTES

Synthesis and Properties of Polycarbosilanes by Hydrosilylation Polymerization

Manabu TSUMURA,* Takahisa IWAHARA, and Toshifumi HIROSE

*Kobe Laboratories, Research Institute, Kaneka Corporation,
1-2-80, Yoshida-cho, Hyogo-ku, Kobe 652, Japan*

(Received March 24, 1995)

KEY WORDS Polycarbosilane / Hydrosilylation / Thermal Stability /
Solubility / Vinyl End-blocked Polycarbosilane / Asymmetry of Substituents
/ Molecular Weight Control

Hydrosilylation polymerization has been reported as the well-known reaction which led to polycarbosilanes (PCS)^{1,2} (Scheme 1) and related polymers.³⁻⁵ However, much attention was not paid to the physical properties of the polycarbosilanes thus prepared.

For instance, the synthesis of PCS **1** ($R^1 = \text{Si(Ph)(Me)-Ar-}$, $R^2 = \text{Ph}$, $R^3 = \text{Me}$; Pt/C cat.; 300°C) was reported by Znamenskaya and co-workers in 1964² (Scheme 1). Under the severe reaction conditions, the yield of PCS **1** was only 30%, the number-average molecular weight (M_n) was around 3000, and the physical properties were not investigated at all.

We recently reported that PCS **2** could be synthesized at room temperature by hydrosilylation polymerization in the presence of the platinum catalyst $[\text{Pt}\{(\text{CH}_2=\text{CHSiMe}_2)_2\text{O}\}_2]$ ^{6,7} (Scheme 2).⁸ In the synthetic reaction in toluene, PCS **2** was precipitated because of the PCS **2**'s low solubility. Actually, minimum

solvent volume required for dissolving 1 g of PCS **2** was above 200 ml at 15–20°C (Table II), and the solubility for the low-molecular-weight derivatives of PCS **2** ($M_n = \sim 10^3$) was low, too. The low solubility seems to be a disadvantage on moldability, such as spinning fibers, forming films, and making a solution for prepreps etc., and also on improvement of physical properties by curing reaction. However the thermal stability of PCS **2** was good (Table II). Our previous work made clear that the unit of $[-\text{Me}_2\text{Si}-p\text{-C}_6\text{H}_4-\text{Me}_2\text{Si}-\text{CH}_2\text{CH}_2-]$ was necessary unit for good thermal stability.

We designed the PCS **1a–c** which was expected to have high solubility owing to the

Scheme 1.

1a–c : $\text{R} = \text{Ph}$
2 : $\text{R} = \text{Me}$

Scheme 2.

* To whom correspondence should be addressed.

asymmetry of their substituents still maintaining good thermal stability because of its backbone structure (Scheme 2).

In this paper, we investigated the synthesis and properties of PCS **1a–c** and vinyl-end blocked PCS **1c**.

EXPERIMENTAL

Materials and Instruments

Diethoxymethylphenylsilane, 1,4-dibromobenzene, Mg, and vinylmagnesium-bromide were purchased from commercial sources. Tetrahydrofuran and toluene were dried over Na/benzophenone and were distilled before use. The platinum catalyst $[\text{Pt}\{(\text{CH}_2=\text{CHSiMe}_2)_2\text{O}\}_2]$ (1.0 wt% xylene solution) was prepared by the reaction of $\text{H}_2\text{PtCl}_6 \cdot \text{H}_2\text{O}$ and 1,1,3,3-tetramethyl-1,3-divinyl-disiloxane.

^1H , ^{13}C , ^{29}Si NMR spectra were recorded in CDCl_3 on a Varian Gemini 300 instrument. Mass spectra were obtained on a Shimadzu GCMS QP-2000A. Gel permeation chromatographic analyses (GPC) were carried out on Waters LC Module with Shodex 804 by using chloroform as an eluent after calibration with standard polystyrene samples. Thermogravimetric analyses (TGA) were made on a Shimadzu TGA50 instrument ($20^\circ\text{C min}^{-1}$) under nitrogen stream (30 ml min^{-1}).

Preparations of 3 and 5 (Scheme 3)

The preparations of **3** and **5** were carried out according to the methods previously reported.^{9,10}

Preparation of 4 (Scheme 3)

In a 100-ml two-neck pear-shape flask equipped with a teflon-covered magnetic stirring bar, a dropping funnel, and a reflux condenser were placed **3** (5.0 g, 12.3 mol) and tetrahydrofuran (THF) (20 ml). A THF solution (1.0 M, 27.1 ml) of vinylmagnesiumbromide was placed in the dropping funnel. The reaction mixture was stirred while the solution of vinylmagnesiumbromide was added over

45 min. After the addition the mixture was stirred for 3 h under reflux and for 16 h at room temperature. Hexane and water were added to reaction mixture. The organic layer was separated and washed with brine. The organic layer was dried over anhydrous sodium sulfate, then filtered, and the solvents were removed by evaporation under reduced pressure. Kugelrohr distillation (0.5 mmHg, 180–220°C, bath temp) gave 2.98 g (8.1 mmol, 66% yield) of **4**. Mass 370 (M^+ , 6), 355 ($\text{M}^+ - 15$, 40), 147 (100). ^1H NMR (δ , CDCl_3) 0.65 (s, SiCH_3 , 6 H), 5.81 (dd, vinyl proton, $J=3$, 21 Hz, 2H), 6.21 (dd, vinyl proton, $J=3$, 15 Hz, 2H), 6.49 (dd, vinyl proton, $J=15$, 21 Hz 2H), 7.37–7.57 (m, aromatic protons, 14H), ^{13}C NMR (δ , CDCl_3) –4.18 (CH_3Si), 127.90, 129.39 (vinyl carbons), 134.16, 134.88, 135.03, 135.73, 136.11, and 137.45 (aromatic carbons), ^{29}Si NMR (δ , CDCl_3) –14.64.

Preparation of PCS 1a (Scheme 2)

In a 30-ml two-neck pear-shape flask equipped with a teflon-covered magnetic stirring bar, a rubber septum and a reflux condenser were placed **4** (1.16 g, 3.1 mmol), 1.0 wt% solution of Pt complex (7.54 μl , 6.3×10^{-4} mmol) and toluene (3 ml). A THF solution (3 ml) of **5** (0.94 g, 3.0 mmol) was added slowly by a syringe at room temperature. After the addition the mixture was stirred for 24 h at room temperature. The solvents were removed by evaporation under reduced pressure, and then white solid (1.96 g) was obtained in an isolated yield of 94%. The crude product was dissolved in a minimum amount of toluene (*ca.* 3 ml) and the polymer was precipitated from hexane. The polymer, 0.91 g (61% yield) was dried under vacuum at room temperature. From GPC analysis, $M_w/M_n = 12500/7000$ was obtained. ^1H NMR (δ , CDCl_3) 0.51 (br s, SiCH_3 , 6H), 1.00 (br s, SiCH_2CH_2 , 4H), 7.27–7.44 (m, aromatic protons, 14 H).

Determination of the PCS **1c**'s Terminal Vinyl Groups

The PCS **1c** isolated by the same process as described above was dissolved in a minimum amount of CHCl_3 (ca. 3 ml) and the polymer was precipitated from methyl alcohol (82% yield). ^1H NMR spectrum of PCS **1c** thus precipitated is shown in Figure 1. This spectrum includes 1,2-dibromoethane as an internal standard. The amounts of 1,2-dibromoethane and the precipitated PCS **1c** were 2.69 mg (*X*) and 50.62 mg (*Y*), respectively. The integral values of methylene groups of 1,2-dibromoethane and vinyl groups of the precipitated PCS **1c** were 1.6 (*A*) and 1.8 (*B*), respectively. From the eq 1,

$$(X/187.9)/(Y/(370 + 344n)) = (A/4)/(B/6) \quad (1)$$

the number of repeated units of the precipitated PCS **1c** was 13.

^1H NMR (δ , CDCl_3) 0.57 (s, SiCH_3), 0.58 (s, SiCH_3), 0.66 (s, SiCH_3), 0.68 (s, SiCH_3), 1.06 (br s, SiCH_2CH_2), 3.65 (s, $\text{BrCH}_2\text{CH}_2\text{Br}$), 5.83 (m, vinyl proton), 6.23 (m, vinyl proton), 6.48 (m, vinyl proton), and 7.27–7.57 (m, aromatic protons).

Scheme 3.

RESULTS AND DISCUSSION

Monomer Synthesis

1,4-Bis(methylphenylvinylsilyl)benzene **4** and 1,4-bis(methylphenylsilyl)benzene **5** were prepared by Scheme 3.

The reaction between $\text{PhMeSi}(\text{OEt})_2$ and 1,4-dibromobenzene exclusively afforded 1,4-bis(ethoxymethylphenylsilyl)benzene **3**. The corresponding reaction of PhMeSiCl_2 , however, did not give 1,4-bis(chloromethylphenylsilyl)benzene at all. That is because the latter reaction was vigorous enough to partly give further-reacted products and the desirable product was easily hydrolyzed during work-up process.

Hydrosilylation Polymerization between **4** and **5**

The PCS **1a–c** were synthesized by hydrosilylation polymerization of bifunctional monomers (Scheme 2). The reaction proceeded quantitatively and homogeneously at room temperature. The reaction was catalyzed by $[\text{Pt}\{(\text{CH}_2=\text{CHSiMe}_2)_2\text{O}\}_2]$.

Table I summarizes the results of the polymerization. The molecular weights of PCS were successfully controlled by changing the molar ratio of **4/5**. The number-average molecular weights (M_n) of PCS **1** were around $1.2\text{--}7.0 \times 10^3$. Although the cyclic derivatives are possible to form in this reaction, we can not exclude the possibility at the present.

^1H NMR spectrum of the PCS **1a** is shown in Figure 1. The resonance signals at 0.51, 1.00, and 7.24–7.44 ppm are assigned to methyl,

Table I. Hydrosilylation polymerization^a between **4** and **5**

Run		4/5 ^b	Solvent [M] ^c	Reaction condition	M_n (M_w/M_n) ^d	Yield/% ^e
1	1a	1.1	Toluene (1.0)	r.t. 24 h	7000 (1.8)	61
2	1b	1.3	Toluene (0.9)	r.t. 24 h	5900 (1.7)	45
3	1c	1.5	Toluene (1.0)	r.t./4 h–85°C/4 h	1200 (1.8)	82

^a The platinum catalyst $[\text{Pt}\{(\text{CH}_2=\text{CHSiMe}_2)_2\text{O}\}_2]$ (1×10^4 equiv rel to the vinyl substituents). ^b Molar ratio of **4** and **5**. ^c Concentration of monomers. ^d Relative values to polystyrene standards obtained by GPC detected on RI after precipitation. ^e The values after precipitation.

Figure 1. 400 MHz ^1H NMR spectra of PCS in CDCl_3 (upper, PCS **1a**, lower, PCS **1c** in the presence of $\text{BrCH}_2\text{CH}_2\text{Br}$).

methylene, and aromatic groups, respectively. The integral ratio of methyl groups/methylene groups/aromatic groups of PCS **1a**, 3/2/8, was almost equal to the calculated value, 3/2/7. Thus the polymerization reaction proceeded quantitatively with β -addition regioselectivity, and the PCS **1a** actually is composed of $[-(\text{Ph})(\text{Me})\text{Si}-p\text{-C}_6\text{H}_4-(\text{Ph})(\text{Me})\text{Si}-\text{CH}_2\text{CH}_2-]$ as repeated units.

Vinyl end-blocked polycarbosilane **1c** was prepared from excess (1.5 equiv) amounts of vinylsilane monomer **4**. The vinyl functionality of the precipitated PCS **1c** could be clearly identified by ^1H NMR as shown in Figure 1. From the calculation by internal standard, the number of repeated units of PCS **1c** was 13 ($M_n=4800$, see EXPERIMENTAL). This calculated value was larger than the observed value by GPC ($M_n=1200$, $n=4$). Thus the absolute molecular weight of PCS **1c** might be larger than the observed one by GPC; for example, the absolute molecular weights by light-scattering of polysilanes, regarded as one of the silicon-based polymers, were reported larger by 2–3 times than the values by GPC.¹¹ It was also clear that the vinylsilane monomer **4** in the precipitated PCS **1c** was partially left by GPC analysis (ca. 5%). The cause of the monomer remaining may be explained by

probability; roughly speaking, the probability of the vinyl functionality unreacted should be 1/9 ($1/3 \times 1/3$) if the reactivity is constant during the reaction.

The PCS **1c** can be further applied for a crosslinking system with a multi-functional SiH compound by hydrosilylation¹². The synthetic route may prove a useful route to give a vinyl-end blocked polycarbosilanes with controlled molecular weights, whereas Znamenskaya's route² did not provide such a controlled polymer.

Physical Properties of Polycarbosilane **1a**

Table II summarizes the physical properties of PCS **1a** compared with PCS **2**.

It was clear that the solubility of PCS **1a** in an organic solvent was much better than that of PCS **2**. We considered the reason why the PCS **1a** was composed of Si atom of chiral center to decrease the crystallinity. The lower melting point of PCS **1a** was caused by the lowering of the crystallinity. The similar effect was reported in the case of polysilanes; $(\text{PhMeSi})_n$ was soluble in organic solvents whereas $(\text{Me}_2\text{Si})_n$ was insoluble in organic solvents.^{13,14}

The thermal stabilities of PCS **1a** and PCS **2**, both of which have almost the same

Table II. Physical properties of polycarbosilanes

Run	Structure	mp/°C	Solubility/ml g ^{-1a}			<i>T</i> _{ds} /°C	TGA wt loss/% ^b	
			CHCl ₃	THF	Toluene		400°C	500°C
1	<p style="text-align: center;">1a</p>	90–95	5	10	10	419	3.4	16.9
2	<p style="text-align: center;">2^c</p>	182–184	> 200	> 200	> 200	360	11.4	27.6

^a Minimum solvent volume required for dissolving 1 g of the polymer at 15–20°C. ^b Under N₂, 20°C/min⁻¹. ^c $M_n = 7300$ ($M_w/M_n = 1.7$).

molecular weight ($M_n \approx 7000$), are shown in Table II together with their TGA curves in Figure 2. It was clear that PCS **1a** was more stable than PCS **2** over the 300–500°C region, which is easily recognized from the TGA curves. The thermal degradation of the polycarbosilanes seems to be caused by the elimination of substituent groups. In general, thermal degradation of polycarbosilanes mainly have two paths; one is elimination of substituent groups and the other is decomposition of backbone. Provided the decomposition of the backbone of PCS is more predominant and the mechanism of the two polymers' decomposition are the same, the (Ph)(Me)Si units in PCS **1a** will be eliminated and will be the Me₂Si units in PCS **2**. As a result, PCS **1a** should be less stable than PCS **2**. These results, however, are not consistent with experimental data (Table II). Accordingly, the elimination of the substituent groups of PCS must be more probable than the decomposition of the backbone. Moreover, the elimination of Me groups of PCS **2** is more likely than that of Ph groups from an estimation based on the bond energies previously reported.¹⁵ If the all methyl groups (two per unit of PCS **1a** and four per unit of PCS **2**) are eliminated, the weight loss

will be calculated 9% (PCS **1a**) and 27% (PCS **2**), respectively. These calculation results seem to be consistent with experimental data (Table II). We are now under way for clarifying thermal degradation behavior of PCS **1a** and PCS **2** by Pyrolysis-Gas Chromatography.

Acknowledgments. This work was performed by Kaneka Corporation, under the management of the Japan High Polymer Center as part of Industrial Science and Technology Frontier Program supported by New Energy and Industrial Technology Development Organization.

REFERENCES

1. J. W. Curry, *J. Am. Chem. Soc.*, **78**, 1686 (1956).
2. E. N. Znamenskaya, N. S. Nametkin, N. A. Pritula, V. D. Oppengeim, and T. I. Chernysheva, *Neftekhimiya*, **4**, 487 (1964).
3. Y. Pang, S. Ijadi-Maghsoodi, and T. J. Barton, *Macromolecules*, **26**, 5671 (1993).
4. P. R. Dvornic and V. V. Gerov, *Macromolecules*, **27**, 1068 (1994).
5. P. R. Dvornic, V. V. Gerov, and M. N. Govedarica, *Macromolecules*, **27**, 7575 (1994).
6. G. Chandra, P. B. Hitchcock, M. F. Lappert, and P. Y. Lo, *Organometallics*, **6**, 191 (1987).
7. P. B. Hitchcock, M. F. Lappert, and N. J. W. Warhurst, *Angew. Chem., Int. Ed. Engl.*, **30**, 438 (1991).
8. K. Ando, J. Kotani, T. Iwahara, and K. Yonezawa, *Jpn. Kokai Tokyo Koho JP06, 287308* (1994).
9. L. W. Breed and R. L. Elliott, *J. Organomet. Chem.*, **9**, 188 (1967).
10. N. S. Nametkin, N. A. Pritula, and T. I. Chernysheva, "Sintez i Svoisiva Monomerov," *Akad. Nauk SSSR, Inst. Neftekhim. Sintez, Sb. Rabot 12-oi [Dvenadtsatoi] Konf. po Vysokomolekul. Soedin.*, 1962, p 97.
11. R. West, *Journal of Organometallic Chemistry*, **300**, 327 (1986).
12. This will be published elsewhere.
13. J. D. Wesson and T. C. Williams, *J. Polym. Sci., Polym. Chem. Ed.*, **18**, 959 (1980).
14. R. E. Trujillo, *J. Organomet. Chem.*, **C27**, 198 (1980).
15. R. Walsh, *Acc. Chem. Res.*, **14**, 246 (1981).

Figure 2. TGA curve of PCS **1a** and PCS **2** under nitrogen stream.